ABSTRACT

Conventionally ceramic grinding media are produced using powder compaction methods. Fabrication of high quality, fine grinding media (diameter less than 1mm) via powder compaction has certain limitations in the processing parameters such as variations in size, density, strength and shape, since even a slight change in any of the processing parameter leads to drastic structural changes. In order to overcome these limitations, a novel processing technique based on sol-gel route has been developed to produce near-net-shaped proto-type zirconia minispheres (~1mm) with required properties that could potentially be used as grinding media.

Sol-gel synthesis has the advantage of being able to prepare ceramic shaped component without the use of powder processing. With this method, impurities are avoided and there is a greater control of the processes at the molecular level. In the present study, this great advantage of sol-gel method is exploited to prepare the ultra fine grinding media of required size and property. Stress induced transformation toughening property of zirconia has been exploited for preparing high quality minispheres. Special attention has been paid to the processing parameters such as viscosity, pH, sintering temperature, heating rate, soaking time, binder ratio and stabilizer concentration etc., since these parameters dictate the structural, physical and mechanical properties of zirconia minispheres.

Transparent, physical and thixotropic zirconium oxalate sol has been prepared by oxalate gelation from metal salts of chlorides, nitrates and
oxalic acid with the pH of the sol adjusted to 1.5 by the addition of nitric acid. The required viscosity (15cPs) of the sol has been attained by the appropriate addition of a suitable organic binder (PVA) ideal for forming zirconia minispheres in a setting solution by extrusion method. The gelled minispheres have been dried at room temperature and subsequently sintered at 1500°C for 5 hours.

Zirconia minispheres without the addition of stabilizer fail to retain the shape and strength after sintering. This destructive effect has been attributed to extensive microcracking caused by the anisotropic volume expansion accompanying the tetragonal to monoclinic transition. The green density of the minispheres is 48% TD and that of the sintered zirconia minispheres prepared without sintering additives is only 82% TD.

In order to overcome the difficulties encountered in undoped zirconia, stabilizing the zirconia minispheres with tetragonal phase is essential which has been attained by adding suitable stabilizing agents. Three types of minispheres namely ceria, yttria, and magnesia stabilized zirconia minispheres have been prepared. The heat treatment has been performed stage by stage in steps of 200°C from 300°C upto 1500°C to analyze the property variation of 13 mol % ceria stabilized zirconia (13Ce-ZrO₂), 5 mol % yttria stabilized zirconia (5Y-ZrO₂) and 8 mol % magnesia stabilized zirconia (8Mg-ZrO₂) minispheres. The stabilized zirconia minispheres have also been extensively characterized by varying stabilizer content with different mol %: ceria (9 to 15 mol %), yttria (3 to 8 mol %) and magnesia (5 to 10 mol %).
The viscosity and pH variation of the sol as a function of time have been observed. In order to study the effect of heating rate on the sinterability, slow (5°C/min) and fast (10°C/min) heating rates have been adopted. Density increases gradually with increase in stabilizer content and reaches a maximum in the range of 93-96 % TD for all the stabilized zirconia minispheres sintered at 1500°C. In contrast, 5Y-ZrO$_2$ minispheres attained maximum density with complete tetragonal phase at a sintering temperature of 900°C. It has been observed that porosity decreases with increase in stabilizer content and sintering temperature.

Thermal decomposition and phase transition studies are discussed in detail by means of TGA and DTA analysis. Variations in percentage of weight loss, shrinkage and porosity with gradual increase in temperature have been analyzed in detail. Surface area analysis using BET technique and FT-IR characterization of all the stabilized dried minispheres have been carried out. FT-IR characterization suggests that the addition of dopant ions does not affect the structure of the zirconyl oxalate.

From X-ray diffraction studies, crystallization and phase transformation behavior of all the stabilized zirconia minispheres have been analyzed by varying the stabilizer contents and sintering temperatures. It has been observed that the tetragonal phase is retained for 13Ce-ZrO$_2$ minispheres sintered at 1500°C for 5 hours, whereas 5Y-ZrO$_2$ and 8Mg-ZrO$_2$ minispheres remained partially stabilized with tetragonal and monoclinic phases for the same sintering temperature. It has been observed that the density and crystallite size increases with sintering temperature while surface area decreases.
Impacts of sintering temperature and stabilizer content on grain growth have been analyzed for all stabilized zirconia minispheres using SEM micrographs. The microstructure of all stabilized minispheres reveals less agglomerated grain growth which results in moderate grain size and very close homogeneous microstructure. It has been observed that the average grain size varies between 0.8 and 2.7 μm for all stabilized zirconia minispheres.

The effect of sintering schedule and stabilizer content on the mechanical properties of all the stabilized zirconia minispheres have been analyzed in detail. It has been observed that even though the hardness increases with stabilizer content and density, it decreases with increase in applied load. Fracture toughness has been found to vary depending on the fraction of tetragonal phase present in the system. It has been observed that the percentage of wear loss slightly increases with milling time and even after 9 hours of milling only negligible contamination has been observed.

In order to reduce the shrinkage and to improve sintered density of the zirconia minispheres, solid loading in the CZO sol has been performed by the addition of t-zirconia powder. It has also been observed that the density of the 13Ce-ZrO₂ minispheres increases with the binder content. A maximum density of 98% TD and hardness of 9.1 GPa have been obtained for the 13Ce-ZrO₂ minispheres prepared using 30 wt% solid loaded zirconium oxalate with the addition of 35 wt% of PVA and sintered at 1500°C for 5 hours.